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The Structure of Isocarborane

by

Hansjuergen Schroeder and George D. Vickers

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The Structure of Isocarborane¹

Sir:

Hoffmann and Lipscomb² recently discussed the potential existence of three geometrical isomers for the icosahedral carborane system. In these structures (Fig. 1) the two carbon atoms are either adjacent (ortho), intermediate (meta), or opposite (para) to each other. To date two parent isomers of this class of compounds have been found which are called carborane^{3,4} and isocarborane.⁵ Efforts for establishing their structures based on chemical and spectral evidence especially by n.m.r. studies have been conducted in this Laboratory.

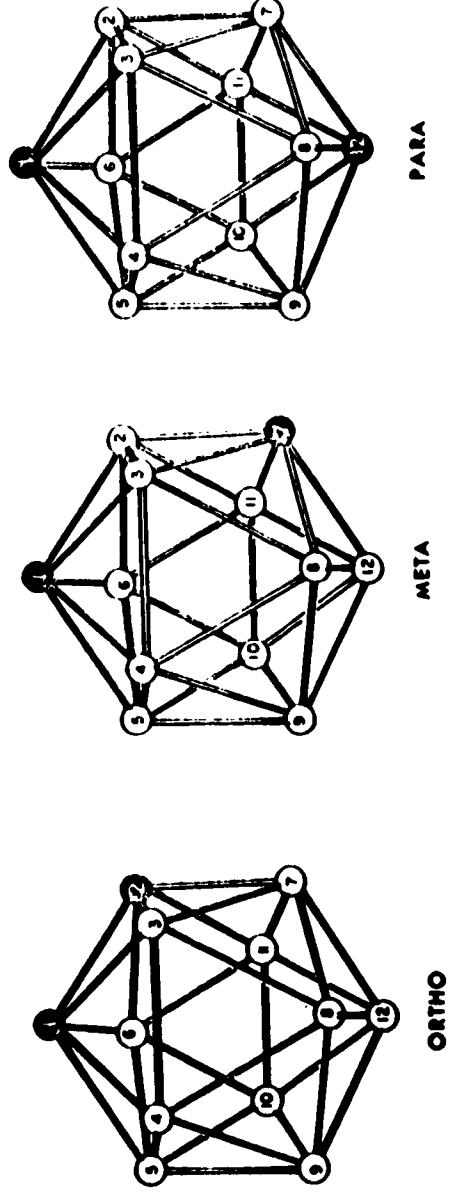
The theoretical ¹¹B n.m.r. spectra of the geometrical isomers can be qualitatively deduced from the environments of the individual boron atoms in their respective icosahedral configurations. All boron atoms of the para-isomer (1,12) are geometrically equal in that each is adjacent to one of the carbon atoms. Therefore the spectrum should consist of only one doublet. The meta-isomer (1,7), on the other hand, has three kinds of geometrically different boron atoms. Two of them (2,3) are affiliated with both carbons, six of them with only one carbon, and the remaining two (9,10) have no carbon in their immediate environment. Based upon these assumptions, the spectrum should display three doublets with an intensity ratio of 2:6:2.

In the case of the ortho-isomer (1,2) we have, in contrast to the other structures, two adjacent carbon atoms. Again two of the boron atoms (3,6) are distinguished by their affiliation with both

-
- (1) Nomenclature and numbering are in accord with the tentative scheme proposed by the Committee on Inorganic Nomenclature.
 - (2) R. Hoffmann and W.N. Lipscomb, *Inorg. Chem.*, 2, 213(1963).
 - (3) T.L. Heying, J.W. Ager, Jr., S.L. Clark, D.J. Mangold, H.L. Goldstein, G. Hillmann, R.J. Polak, and J.W. Szymanski, *Inorg. Chem.*, 2,(1963).
 - (4) M.M. Fein, J. Bobinski, N. Mayes, N. Schwartz, and M.S. Cohen, *Inorg. Chem.*, 2,(1963).
 - (5) D. Grafstein and J. Dvorak, *Inorg. Chem.*, 2,(1963).

Figure 1

ICOSAHEDRAL CARBORANE CONFIGURATIONS



carbon atoms. Of the remaining eight boron atom, four are adjacent to one or the other carbon, and four have only boron atoms in their environment. This rationalization should be reflected in a three doublet spectrum. However, the presence of the unique carbon-carbon bond in this isomer might easily result in a spectrum in which these eight borons appear equal.

As reported recently⁶, we examined the ^{11}B n.m.r. spectra (Fig. 2) of carborane and decachlorocarborane. The former compound displayed two doublets with an area ratio of 2:8. Exchange of all boron bound protons by chlorine atoms in $\text{B}_{10}\text{Cl}_{10}\text{C}_2\text{H}_2$ produced a spectrum of two singlets with an intensity ratio of 2:8. Since these spectra were consistent only with the requirements of the ortho configuration, we assigned this structure to carborane.

We now have examined the ^{11}B spectrum of isocarborane (Fig. 2). It consists of three doublets which can be decoupled into singlets by irradiating with a saturating 60 Mc. field. Since the overlapping of the doublets did not permit the area measurement required for the structure determination, the novel decachloroisocarborane was synthesized by direct chlorination of isocarborane in refluxing carbon tetrachloride in 90% yield, m.p. 235° [calcd. for $\text{C}_2\text{H}_2\text{B}_{10}\text{Cl}_{10}$ (488.8): C, 4.91; H, 0.41; B, 22.14; Cl, 72.54; found: C, 4.95; H, 0.50; B, 22.15; Cl, 72.65; mol. weight: 492.0]. Iso- $\text{B}_{10}\text{Cl}_{10}\text{C}_2\text{H}_2$ exhibited the expected three singlets (Fig. 2) with an area ratio of 2:6:2. Since these findings were consistent with the requirements described above for the meta configuration, we propose to assign this structure to isocarborane.

This conclusion which is based upon nuclear magnetic resonance spectroscopy, reconciles theoretical considerations with the chemistry reported. It was proposed from bonding principles⁷ and molecular

(6) H. Schroeder, T.L. Heying, and J.R. Reiner, *Inorg. Chem.* 2,....(1963)

(7) W.N. Lipscomb, *Proc. Natl. Acad. Sci. U.S.*, 47,1791 (1961).

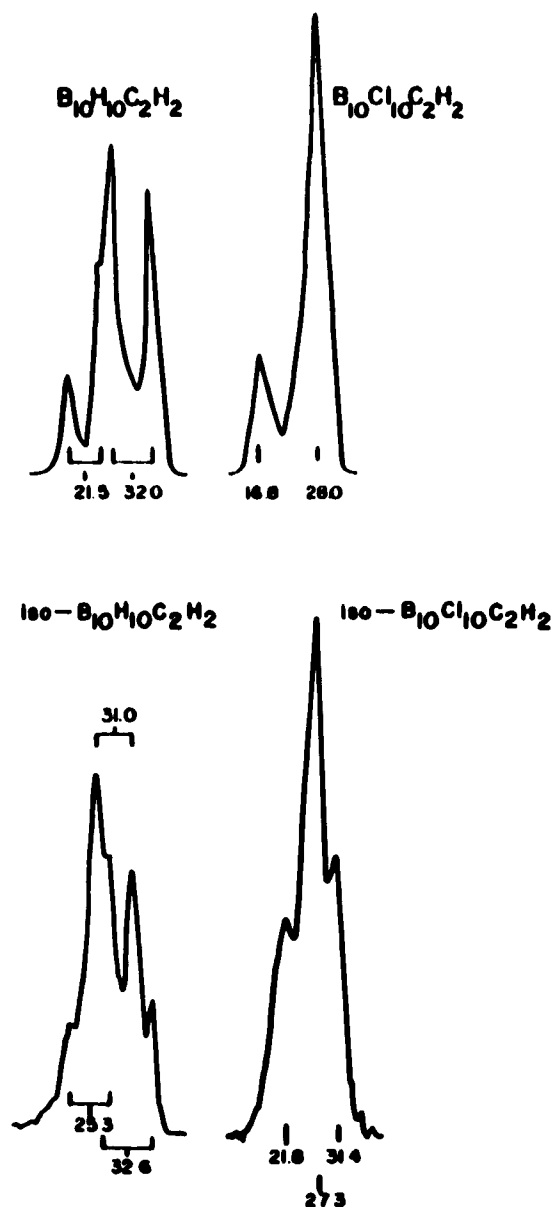


Fig. 2- ^{11}B n.m.r. spectra of two carboranes and two iso-carboranes in acetonitrile in displacement (in p.p.m.) from methyl borate. The chemical shifts of the boron resonance doublets were obtained from the decoupled spectra.

orbital energies⁸ that the meta isomer should be more stable than the ortho isomer. Thus the preparation of isocarborane⁵ which was obtained from carborane at approximately 470°, is in accord with this assumption. As opposed to the participation of carborane in five-membered exocyclic rings^{3,4}, similar reactions of isocarborane⁵ led only to non-cyclic derivatives. Also, comparison of isocarborane derivatives with the analogous carborane derivatives has shown that the former are almost invariably lower melting; this would indicate that the former are of a more unsymmetrical conformation than the latter. From additional work in progress in this Laboratory, we have not encountered any evidence which would contradict this assignment.

(8) R. Hoffmann and W.N. Lipscomb, J. Chem. Phys., 36, 2179 (1962).

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Organics Division
Olin Mathieson Chemical Corporation
New Haven, Connecticut

Hansjuergen Schroeder
George D. Vickers

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